

The Discovery of Polyacetylene Film: The Dawning of an Era of Conducting Polymers (Nobel Lecture)**

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This lecture is not directly related to our discovery and development of conducting polymers to which the Nobel Prize in Chemistry 2000 was awarded. However, I would like to present my previous work that I had

carried out just before we reached the discovery of chemical doping. I hope that this will be of use and deepen your understandings by learning what had happened before and how we reached the idea of chemical doping.

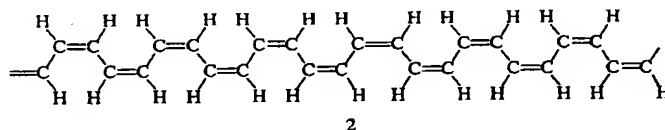
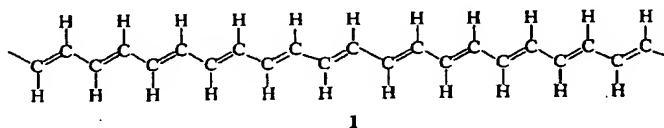
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1. Prologue

It has been recognized for many years that a very long linear-conjugated polyene might have various interesting properties, especially optical, electrical, and magnetic properties. The definition of the polyene is that an even number of methyne ($=CH-$) groups is covalently bonded to form a linear carbon chain bearing one π electron on each carbon atom. Therefore, the chemical structure of the polyene is best represented by a formula $H(CH=CH)_nH$, where n denotes the number of repeating units. Recently *polyacetylene* has become a more popular name than polyene because polyacetylene, synthesized by the polymerization of acetylene, has been used extensively as specimens for various studies.

Pople and Walmsley described in their article in 1962^[1] that “Although it is not possible to synthesize very long polyenes (polyacetylene) at present, general interest in conjugated polymers with related, but rather more complex, structures makes a full study of the electronic states of this simple polymer worthwhile”. Although the first polymerization of acetylene was reported in no later than 1958 by Natta and co-workers,^[2] who prepared polyacetylene that is structurally identical to the very long conjugated polyene, the work was not accepted widely in the field. Before that time interest in this compound was limited, for chemists, to theoretical approaches to explain a red-shift of absorption maximum (bathochromic effect) and an increase in absorption coefficient (hyperchromic effect)

with increasing the number of repeating units in the conjugation, and to elucidate bond alternation in connection with an electron–phonon interaction for physicists. An accumulation of experimental observations on relatively short polyenes^[3–8] coupled with theoretical considerations such as the free-electron model and simple Hückel molecular orbital treatments strongly suggested that the difference between the lengths of double and single bonds decreases with increasing the conjugation and that all the bonds tend to be of equal length in an infinitely long polyene. In other words, one would expect that the infinitely long, one-dimensional arrangement of π electrons forms a half-filled band, or that the highest occupied (HO) and the lowest unoccupied (LU) π -electron bands merge with each other, leading to metallic behavior.^[9, 10] In the 1950s, however, it became theoretically clear that the polyene with bond alternation is energetically more stable than that with bonds of equal length.^[1, 11–13] Since two geometrical isomers, *trans* and *cis*, are possible for each double bond, two isomeric forms, all-*trans* (**1**) and all-*cis* (**2**), are expected as the two extremes of polyacetylene isomers. Experimentally the carbon–carbon bond lengths in poly-



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acetylene were directly measured by Yannoni and Clarke^[14] with use of the nutation NMR spectroscopy, 1.36 and 1.44 Å for the double and single bonds, respectively, in the *trans* form and 1.37 Å for the double bond in the *cis* form.

Even after the first synthesis by Natta and co-workers,^[2] polyacetylene remained for some time a material of interest to only a few organic^[15, 16] and polymer chemists^[17–19] because the product was obtained as insoluble and infusible powders.

2. *trans* or *cis*?

Among the few chemists working on polyacetylene, S. Ikeda and co-workers had been studying a mechanism of acetylene polymerization in connection with olefin polymerization by various Ziegler–Natta catalysts. They found that the polymerization yields not only highly polymerized polyacetylene but also benzene, that is, a cyclic trimer of acetylene, and that the ratio of these two products depends upon species of Ziegler–Natta catalyst used. They also found the formation of alkylbenzenes as a minor by-product of the acetylene polymerization with a catalyst system composed of titanium tetrachloride and trialkylaluminum. In a series of experiments using carbon-14 and deuterium, they noted that a labeled ethyl group is introduced in the ethylbenzene when triethylaluminum labeled with carbon-14 or deuterium is used as the co-catalyst.^[20] In other experiments on the oxidation of polyacetylene by alkaline potassium permanganate, they observed the formation of propionic and acetic acids that are derived from the alkyl groups in the trialkylaluminum used as the co-catalyst.^[20] From these results, they concluded that polyacetylene and benzene could be formed from the same active site of the catalyst system. Thus, the reaction proceeds by *cis*-opening of the triple bond in acetylene followed by a *cis* insertion into the titanium–alkyl bond of the catalyst. This mechanism fits the orbital interaction consideration by Fukui and Inagaki,^[21] for the role of the catalyst according to which the initially formed configuration of the

double bond is *cis* as a result of favored orbital interaction between the inserting acetylene and the active site of the catalyst. Whether cyclic trimerization occurs to give benzene or polymerization proceeds to give polyacetylene is determined by the conformation of the growing chain that takes either *cisoid* or *transoid* structure in the vicinity of the active site of the catalyst.^[22] As no *cis* form had been known until then, an important question remained: why is the mechanism capable of yielding only a *trans* configuration of the double bonds in polyacetylene?^[2, 19]

3. Discovery of Film Synthesis

The conventional method of polymerization in the laboratory is such that the catalyst solution is stirred thoroughly to carry out the reaction under homogeneous conditions. The acetylene polymerization has not been an exception: it was customary for polymer chemists who synthesized polyacetylene to bubble acetylene gas into a stirred catalyst solution. Unfortunately, the product was obtained as an intractable black powder that is very difficult to make into samples of a shape suitable for measurement of spectra and physical properties because of its insolubility and infusibility.

In 1967, soon after I joined Ikeda's group, we succeeded in synthesizing polyacetylene directly in the form of a thin film^[23] by a fortuitous error. After a series of experiments to reproduce the error, we noticed that we had used a concentration of the Ziegler–Natta catalyst nearly a thousand times greater than that usually used. It is worth noting that the insolubility of polyacetylene contributes to the formation of the film. In addition, it was found that the film is composed of entangled micro-fibers (called fibrils), this discovery was made by transmission electron microscope observation of an extremely thin film and by scanning electron microscope observation of the surface of a thick film (Figure 1). The fibril diameter is in the range of 20–100 nm depending upon the

Hideki Shirakawa was born in Tokyo, Japan on August 20, 1936. He received his B.S., M.S., and Ph.D. from the Tokyo Institute of Technology. After completion of his Ph.D. in 1966, he joined Professor Sakuji Ikeda's group at the Research Laboratory for Resources Utilization, Tokyo Institute of Technology, where he investigated acetylene polymerization for the elucidation of the polymerization mechanism by Ziegler–Natta catalysts. In 1967, he noticed on formation of polyacetylene in a form of a film with metallic luster following an unforeseeable experimental error by one of his co-workers.



By chance, this silvery film caught the eyes of Professor Alan G. MacDiarmid, he was invited to work in University of Pennsylvania for one year during 1976 and 1977 where they found the chemical doping of acetylene jointly with Professor Alan J. Heeger. In November 1979, he moved from the Tokyo Institute of Technology to the Institute of Materials Science, University of Tsukuba, where he was appointed Associate Professor. In October 1982, he was promoted to full professor and worked on polyacetylene and other conducting polymers. He retired from the University of Tsukuba at the end of March 2000. He is currently a member of Council for Science and Technology Policy, Cabinet Office. He received the Award of the Society of Polymer Science, Japan in 1983, Award for Distinguished Service in Advancement of Polymer Science, from the Society of Polymer Science, Japan in 2000, the Order of Culture in 2000 from Japanese Government, and the Nobel Prize for Chemistry in 2000.

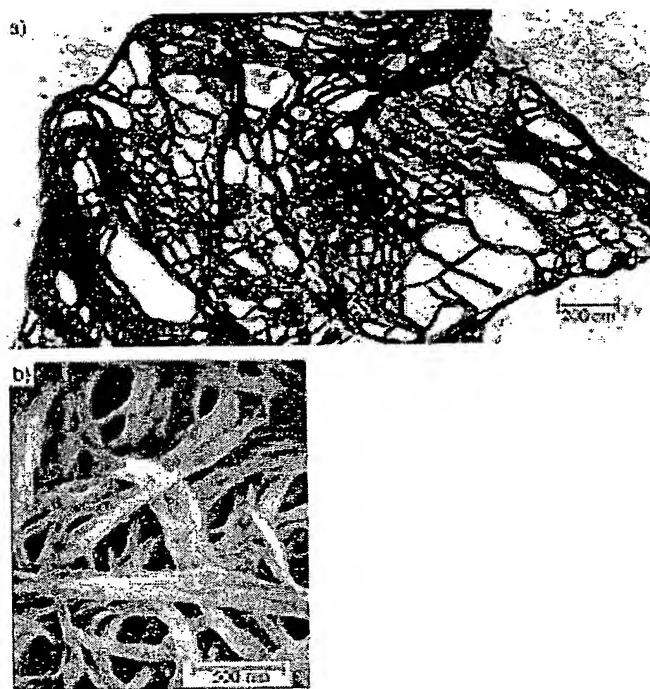


Figure 1. a) Transmission electron micrograph of an extremely thin film of polyacetylene. b) Scanning electron micrograph of the surface of a thick polyacetylene film.

polymerization conditions. These inherent properties of polyacetylene are absolutely necessary for the film formation even under the higher concentration of the catalyst. One more important factor that should be added is that the catalyst used at that time, $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4/(\text{C}_2\text{H}_5)_3\text{Al}$, was quite unique from the viewpoint of its good solubility in organic solvents, such as hexane or toluene, to give a homogeneous solution, and its high activity to give exclusively high molecular weight and crystalline polymers. On the contrary, most Ziegler–Natta catalysts form precipitates to give inhomogeneous solutions when a titanium compound is mixed with alkylaluminum.

The use of the films enabled us to obtain clear infrared spectra, as shown in Figure 2,^[24] and analysis of these spectra indicated that the configuration of the double bonds strongly depends on the temperature of polymerization. The *trans* contents of polyacetylene prepared by the Ziegler–Natta catalysts decreases with decreasing polymerization temperature (Table 1). Thermal study^[25] indicated that the irreversible isomerization of the *cis* form occurs at temperatures higher than 145 °C to give the *trans* form. Thus

Table 1. The *trans* contents of polyacetylene prepared at different temperatures T [°C]

T [°C]	<i>trans</i> Content [%]	T [°C]	<i>trans</i> Content [%]
150	100.0	0	21.4
100	92.5	–18	4.6
50	67.6	–78	1.9
18	40.7		

[a] Catalyst: $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4/(\text{C}_2\text{H}_5)_3\text{Al}$, $\text{Ti}/\text{Al} = 4$, $[\text{Ti}] = 10 \text{ mmol L}^{-1}$.

the *cis* form is thermodynamically less stable than the *trans* one. The observed *cis*-rich polyacetylene synthesized at lower temperatures suggested the *cis*-opening of the triple bond of the acetylene monomer consistent with the *cis*-opening mechanism proposed by Ikeda.^[22] In case of the polymerization being carried out at higher temperatures, spontaneous isomerization of the growing chain of *cis* double bonds occurs to give *trans* ones, also consistent with the *cis*-opening mechanism proposed by Ikeda.^[22] The *cis*-opening mechanism has been supported by the nutation NMR study^[14] and by the infrared study of copolymers of acetylene and $[\text{D}_2]$ acetylene.^[24] In conclusion, the open problem why only *trans* polyacetylene had been known was solved by the use of films.

4. Electrical Properties of “As-Prepared” Polyacetylene Films

The electrical resistivity of “as-prepared” (untreated) films with various *cis/trans* contents was measured by the conventional two-probe method under vacuum in a temperature

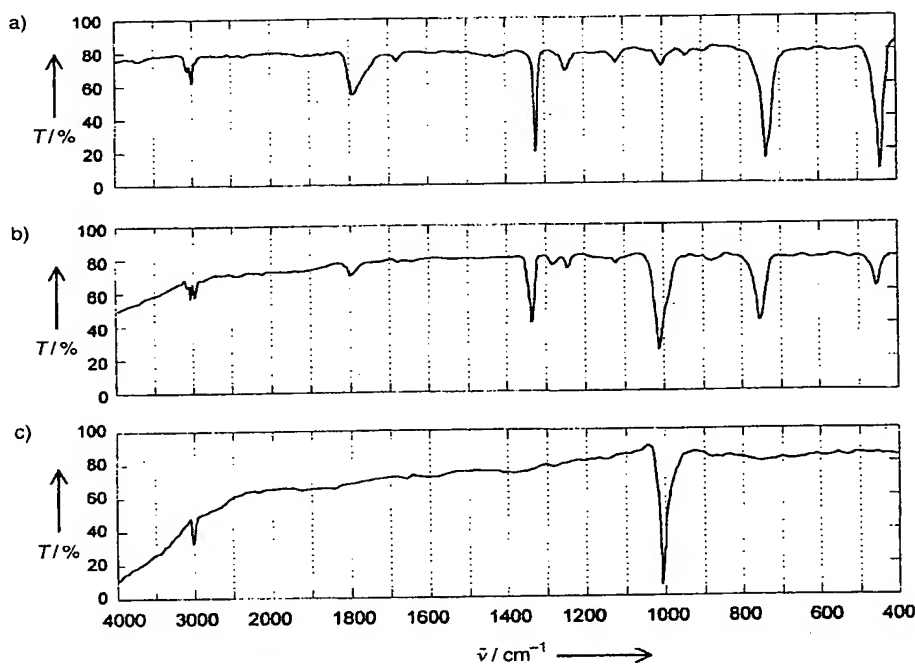


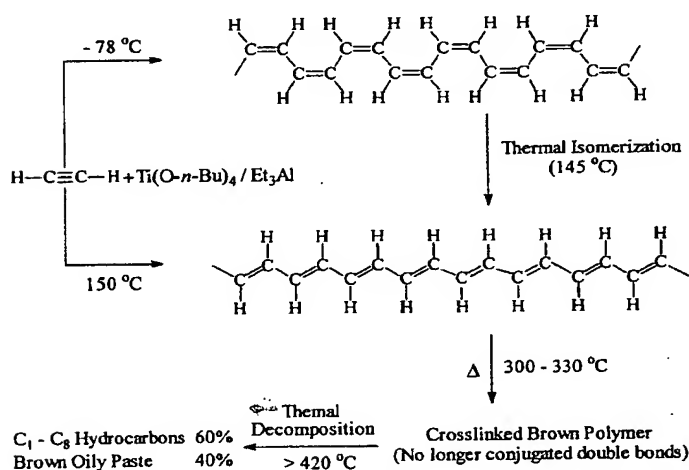
Figure 2. Infrared spectra of polyacetylene synthesized at a) –78 °C, b) 20 °C, and c) 150 °C. Cf. ref. [24], Figure 4.

range of -120 – $+20^{\circ}\text{C}$.^[26] The resistivity and energy gap of *trans*-rich polyacetylenes were $1.0 \times 10^4 \Omega\text{cm}$ and 0.56 eV , respectively, whereas the values of a *cis*-rich (80%) one were $2.4 \times 10^8 \Omega\text{cm}$ and 0.93 eV , respectively. Hatano et al.^[17] reported that the resistivity and energy gap measured on compressed pellets of powder polyacetylene synthesized by the same catalyst system are in the range of 1.4×10^4 and $4.2 \times 10^5 \Omega\text{cm}$, and 0.46 eV , respectively, in good agreement with those for *trans*-rich polyacetylene film. In conclusion, it became apparent that the intrinsic electrical properties do not change very much between powder and film.

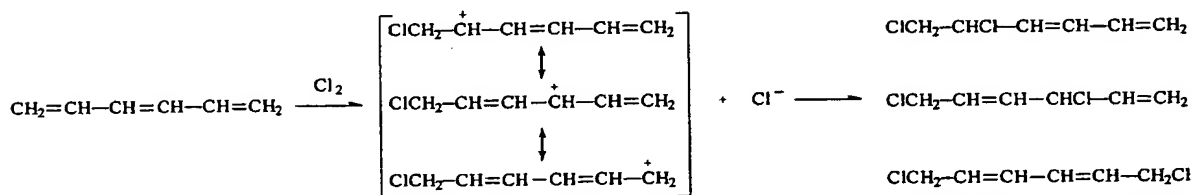
5. Halogenation of the Polyacetylene Films

Since no improvement in electrical conductivity was observed in film form, we tried to use the polyacetylene films as a source of graphite films as the carbon content of the polymer is as high as 92.3%. Thermograms from differential thermal analysis of *cis*-rich polymer revealed the existence of two exothermic peaks at 145 and 325°C and one endothermic peak at 420°C which were assigned to *cis*–*trans* isomerization, hydrogen migration accompanied with cross-linking reaction, and thermal decomposition, respectively^[23] (Scheme 1). Thermogravimetric analysis showed that weight loss reached 63% at 420°C . Therefore, pyrolysis of as-prepared polyacetylene films is not suitable for the preparation of graphite films.

Electrophilic addition of halogens such as chlorine and bromine to a carbon–carbon double bond is a well-known



Scheme 1. Thermal characteristics of polyacetylene.



Scheme 2. Possible resonance structures for the intermediate during the chlorination of 1,3,5-hexatriene to give three chlorinated products.

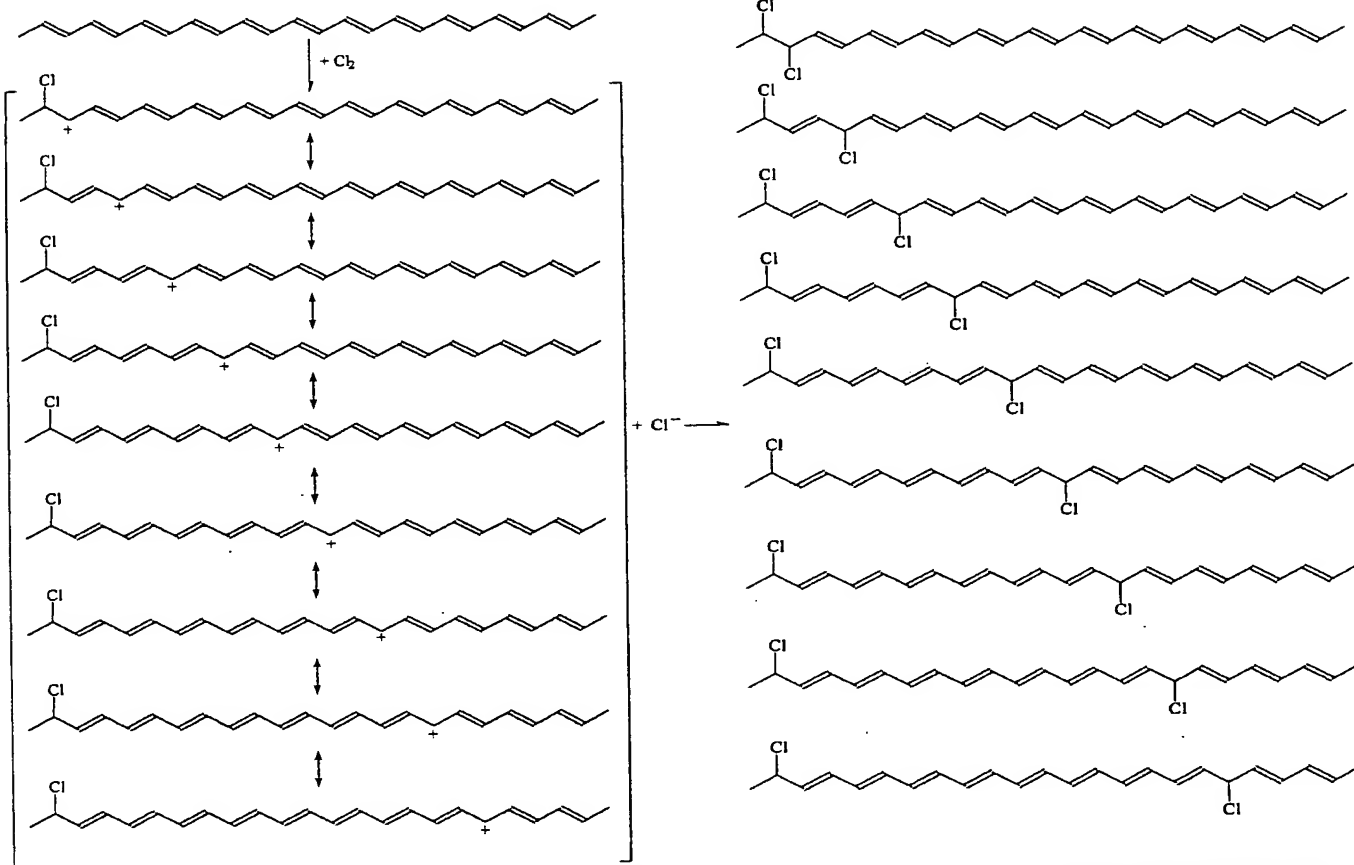
reaction and proceeds with good yield and few side reactions. Elimination of hydrogen halide from adjacent carbon atoms in a halogenated hydrocarbon is also a well-known reaction to introduce a carbon–carbon double or triple bond. Since polyacetylene reacts with chlorine and bromine under mild conditions, we thought carbonization might be possible by combining the both reactions. Thus, a polyacetylene film was treated with chlorine at room temperature to give a chlorinated polyacetylene film, which was subsequently treated with a basic reagent to eliminate hydrogen chloride to give a carbon film in satisfactory yield. However, we found that the carbon film was hardly graphitized even when heated at 2000°C for several hours.

Fully chlorinated polyacetylene has a chemical structure of $-(\text{CHCl}-\text{CHCl})_n-$, corresponding to a polymer of 1,2-dichloroethylene. It is known, however, that 1,2-disubstituted ethylenes hardly ever polymerize. Therefore, the chlorination of polyacetylene is the sole method to synthesize poly(1,2-dichloroethylene). To investigate the chlorination process of the polyacetylene film, in situ measurements were planned to obtain infrared spectra during the chlorination of the polyacetylene film.

It is well known that chlorination of the simplest conjugated polyene, 1,3-butadiene, gives two isomeric products, the 1,2-addition product (3,4-dichloro-1-butene) and the 1,4-addition product (1,4-dichloro-2-butene). Likewise, 1,3,5-hexatriene gives three isomers, 1,2-, 1,4-, and 1,6-addition products. The reason why the reaction gives various products is explained by the existence of different resonance structures in the intermediate (Scheme 2). The third isomer is thermodynamically the most stable because the molecule has an inner conjugated diene structure with the largest energy of resonance stabilization.

The motivation for the study was to confirm that the 1,2n-addition of chlorine might occur as the initial step of the reaction as shown in Scheme 3. Since the longer inner polyene structure has the larger energy of resonance stabilization, it is anticipated that products of 1,2n-addition with larger n predominate, rather than a 1,2-addition product at the initial step of the reaction or in the partially chlorinated polyacetylene. If such structures could be detected by infrared spectroscopy, one might expect that the positive charge on the intermediate carbocation is able to migrate far away from the reaction site through the conjugated polyene structure.

Contrary to this expectation, the infrared spectrophotometer recorded no spectrum but only a 100% absorption line in the full range of 4000 to 400 cm^{-1} immediately after addition of a trace amount of chlorine to the film. The polyacetylene film changed into an opaque material because



Scheme 3. Possible resonance structures for the intermediate in the chlorination of polyacetylene, the expected chemical structures of partially chlorinated polyacetylene are also shown.

of some very strong absorptions. Upon continued reaction with additional chlorine, the spectrum became clearer to give that corresponding to a chlorinated polyacetylene.

6. Epilogue

Later, we know that the very strong absorption is the so-called "doping induced infrared band" composed of three bands at 1397, 1288, and 888 cm^{-1} ,^[27-29] which have extremely strong absorption coefficients compared with those of the as-prepared polymer. The observed isotope shifts of these bands in the spectra of poly($^{13}\text{C}_2$ acetylene) and poly($^{13}\text{C}_2$ acetylene) demonstrated that these bands are of vibrational origin^[27] in the vicinity of the carbocation or positively charged carbon atom in the conjugated polyene. At present, the carbocation formed in long conjugated polyenes is widely known as a positively charged soliton^[30] that acts as a charge carrier for the electrical conduction. At that time, to my regret, I did not recognize that this carbocation could be a charge carrier and thus polyacetylene could be the first conducting polymer. To open an era of conducting polymers, we had to wait until we intentionally carried out the doping

experiment with bromine at the University of Pennsylvania, on Tuesday 23rd, of November 1976, and then later also successively with iodine.^[31, 32]

At the end of my lecture I want to express my heartfelt thanks to the late Professor Sakuji Ikeda who gave me a chance to work on the acetylene polymerization, to Professor Masahiro Hatano who contributed to the semiconducting polymers and encouraged me on my work, to the late Professor Shu Kambara who organized our polymer research group and supported us in our work even after his retirement, and to Dr. Hyung Chick Pyun with whom I encountered the discovery of polyacetylene film by the fortuitous error. Dr. Takeo Ito was the first graduate student to work for me and who made a great contribution at the initial stage of this work. My special thanks are to Professors Shiro Maeda, Takehiko Shimanouchi, and Mitsuo Tasumi for helpful discussion on the vibration analyses study. I am indebted to Mr. Shigeru Ando for measurements of solid-state properties and to Professor Yoshio Sakai for electrical conductivity measurements. Throughout this period, our research was partly supported by Grant-in-Aids for Scientific Research from Ministry of Education, Culture and Science of Japan.

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